katharometer for a given increase in room temperature if the gases had no
temperature coefficient of conductivity,

$$\frac{\text{fractional change in } z/x}{\text{fractional change in } \beta} = \beta \cdot \frac{x}{z} \cdot \frac{d}{d\beta}\left(\frac{z}{x}\right)$$

$$= \frac{1}{(1+\beta/\alpha)+\beta(k+1)/\text{G}}.$$

In the simplest case, where $\alpha = \beta = \text{G}$ and $k = 1$, as we usually have in a
katharometer, this ratio is $\frac{1}{4}$, *i.e.*, if the temperature coefficient of resistance of
the platinum wire is 0·0038 per 1° C. we should expect the sensitiveness of
the bridge to increase by about 0·10 per cent. per 1° C. rise in temperature.
This would tend to reduce the expected fall of 0·30 per cent. in sensitiveness
due to the increase in conductivity of the air and give us a final temperature
coefficient of direct deflection of −0·20 per cent. per 1° C. This is in good
agreement with an experimental value which gave −0·21 per 1° C. The
magnitude of the effect varies, of course, with the bridge arrangement.

The Process of Diffusion through a Rubber Membrane.

By H. A. DAYNES, M.Sc.

Introduction.

The production of balloon and airship fabrics in large quantities during
the war has raised many problems in connection with leakage of hydrogen
through membranes.   It is desirable to have more information about the
process by which gas passes through such rubber membranes.

In considering a rubber film, two alternatives have been suggested. One
is that the chief obstacle to the passage of a gas is that provided by the
material itself, and that the gas can pass the surfaces of the film quite readily.
The other is that the chief obstacle is at the surface, the actual thickness of
rubber having very little effect on the permeability.

The first view has been dealt with by Wroblewski(1) in 1879. He
assumes :

(1) That when a piece of rubber is left exposed to a gas at normal pressure
it absorbs a volume of gas which is a definite fraction of its own volume,
and that this fraction, which he calls the "absorption coefficient," varies
with the temperature of the rubber.

(2) That the absorption is proportional to the partial pressure of the gas.

(3) That when one side of a rubber membrane is exposed to hydrogen and the other to air, at a very short distance from the hydrogen surface, the concentration of gas in the rubber is the same as if the whole piece were immersed in hydrogen, and that a very short distance from the other face the concentration of hydrogen is negligible.

(4) That within the material Fick's Linear Diffusion Law holds as for free gases and liquids, *i.e.*, the nett rate of passage of gas in a given direction varies as the gradient of concentration of gas in that direction.

He therefore expresses the permeability of a fabric by a simple formula

$$Q = KA \frac{p_1 - p_2}{l},$$

where
  Q = quantity passing through the fabric per second.
  K = diffusion constant for the gas in the rubber.
  A = absorption coefficient.
  p_1 and p_2 = partial pressures of the permeating gas at the two sides of the fabric, either being unity when the gas is at normal pressure.
  l = thickness of film.

The other view of the process is expressed in its extreme form in the statement that the permeability of a film is, within wide limits, independent of its thickness, *i.e.*, it can be expressed by a simple formula

$$Q = P(p_1 - p_2).$$

It might be expected that each set of conditions would hold over extreme ranges of very thick and very thin films respectively, and that there would be an intermediate range of thickness where a formula would hold such as

$$Q = \frac{p_1 - p_2}{R + l/KA},$$

where R may or may not be a constant for different values of l. If it were a constant the quantity RKA might be called the "equivalent extra thickness" of the surfaces.

The work done in this laboratory deals only with films from 0·03 to 1·6 mm. in thickness.

In considering evidence, a distinction has to be drawn between the case where a gas permeates through a membrane into a vacuum, and that where it permeates into another gas, because in the latter case there is a simultaneous absorption of the other gas. It remains to be shown to what extent the gases may be considered to act independently.

The following are results of absorption experiments by various workers.

Draper and Mitchell (2), about 1850, found that rubber absorbs about its own volume of carbon dioxide.

Wroblewski (3) in 1879 found the following values of the absorption coefficient A for rubber in strips at a temperature $\theta°$ C. :—

Nitrous oxide   .... $A_\theta = 1·9561 - 0·026649\,\theta$

Carbon dioxide   .... $A_\theta = 1·2779 - 0·015\,\theta$

Hydrogen   .... $A_\theta = 0·02050 + 0·004\,\theta$

Air   .... $A_\theta = 0·06075 + 0·0037\,\theta$

Hüfner (4), in 1888, using grey vulcanised rubber, found no absorption of air except that necessary for oxidation (5° C. to 25° C.), no nitrogen absorption (15° C. to 25° C.), no absorption of hydrogen ($-2°$ C. to $+13°$ C.), but rubber absorbed its own volume of carbon dioxide.

The only point on which these are agreed is that rubber absorbs its own volume of carbon dioxide.

In all these experiments the whole surface of the rubber was exposed to the gas. There is no question of the independence of action of two gases in a mixture. There is, also, no complication due to resistance at the surface. Experiments have, apparently, not yet been done on direct absorption of mixtures of gases. This would be of interest in connection with some permeability results to be described later.

It has been shown (5) that the absorption is proportional to the gas pressure.

When we come to consider the case of one gas diffusing through the membrane into another gas there is much more reliable evidence. The rubber used here was Para, with 5 per cent. litharge and about 3 per cent. sulphur.

1. (*a*) Under these conditions the quantity of hydrogen passing through is proportional to the partial pressure of the gas when one gas is pure air and the other a mixture of hydrogen and air (6) (7).

Also when two fabrics of permeabilities P_1 and P_2 are placed together in series and exposed on the two sides to hydrogen and air respectively, the permeability is $P_1 P_2/(P_1 + P_2)$ (8). This shows that the quantity passing through the fabric is proportional to the difference of partial pressure on the two sides when one gas is pure hydrogen.

Similar tests (9) with three fabrics in series test the case of mixtures on both sides.

(*b*) The temperature coefficient of permeability is, as nearly as could be measured, the same for all differences of partial pressure (10).

2. (*a*) The permeability of a rubber film is approximately inversely proportional to its thickness (11).

(*b*) The temperature coefficient of permeability is, over fairly wide ranges, independent of the thickness of the film (12).

3. (*a*) Work on the permeability of rubber films and rubbered fabrics to various gases (13) (14) shows no obvious correlation between permeability and density or molecular structure of the gas. The rates of passage of nitrogen and oxygen are very different, although they have nearly the same densities and molecular structure. Carbon dioxide and water vapour pass very freely.

(*b*) The temperature coefficient of permeability is not the same for all gases, nor is there any obvious relation between this and other physical constants of the gases (15).

4. With regard to the independence of action of several gases in a mixture :

(*a*) The permeability of rubber to carbon dioxide is the same within 2 per cent. whether hydrogen or air is on the other side of the fabric, over a range of 10° C. to 23° C. (16) ; and

(*b*) The total volume of gas passing through the rubber from nitrogen and oxygen in atmospheric proportions to hydrogen is the same within 2 per cent. over a range of 10° C. to 23° C. as if each gas acted independently according to its partial pressure (17).

It will be seen that all the results here quoted are consistent with the following assumptions :

(1) That Fick's diffusion law holds inside the material ;

(2) That absorption of a gas is proportional to the partial pressure, independently of the presence of any other gases ;

(3) That there is no appreciable resistance at the surface to the passage of the gas ; and

(4) That the different gases present do not appreciably impede one another in passing through the rubber.

If one of these conditions did not hold, the others would have to be adjusted in some complicated way to account for the experimental results.

If these conditions do hold, we can then speak of a definite concentration of hydrogen at a given point in the rubber, and the problem of permeability in films and such membranes become calculables according to the same laws as diffusion of gases through one another.

This has suggested the experiments described later in this paper, in which the time taken to set up steady conditions of passage through a rubber film is used to separate out the parts played by diffusion and absorption of the gas in the whole process.

Theory of the Method.

Evidence has been given in the introduction that the problem of diffusion of hydrogen through rubber may be treated in the same way as the problem of diffusion through a similar space filled with gas.

We can therefore use the differential equation of diffusion

$$Q = -K \frac{dy}{dx},$$

where   Q is the flux of hydrogen in the direction of x in c.c. per second,

K is the " diffusion constant " for hydrogen in the rubber,

y is the concentration of hydrogen at the point x in c.c. of hydrogen at N.T.P. per c.c. of rubber.

This equation is to be applied to each gas, independently of other gases present, using, of course, the appropriate value of K.

As boundary conditions we have at a surface where the partial pressure of hydrogen is p, $y = Ap$ where A is the absorption coefficient of hydrogen in rubber, *i.e.*, the saturation value of y for gas at normal pressure.

It is not possible to obtain from permeability experiments alone any idea of the separate values of K and A. For example, in the case of a uniform sheet of thickness l we have volume of gas passing through per second in the steady state,

$$Q = \frac{KAp}{l}.$$

Measurements of permeability only determine the product KA. But if we measure the time taken to set up a steady state we obtain some information as to the absolute values of K and A.

Consider a uniform film of thickness l. Initially, both faces are exposed to air. At a given instant one face is exposed to hydrogen. It is required to find the rate at which hydrogen is given off from the other face at any given time t.

The general solution for the case where

$$y = y_1 \text{ for } x = 0,$$

$$y = y_2 \text{ for } x = l,$$

and $y = f(x)$ at $t = 0$ is (18),

$$y = y_1 + (y_2 - y_1)\frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{n=\infty} \frac{y_2 \cos n\pi - y_1}{n} \cdot \sin \frac{n\pi}{l} x \cdot e^{-K n^2 \pi^2 t / l^2}$$

$$+ \frac{2}{l} \sum_{n=1}^{n=\infty} \sin \frac{n\pi}{l} x e^{-K n^2 \pi^2 t / l^2} \int_0^l f(x') \sin \frac{n\pi}{l} x' \, dx'.$$

In this special case

$$f(x) = 0, \qquad y_1 = 0, \qquad \text{and} \qquad y_2 = Ap.$$

Therefore, $\quad y = Ap \dfrac{x}{l} + \dfrac{2}{\pi} \overset{n = \infty}{\underset{n=1}{\Sigma}} Ap \dfrac{(-1)^n}{n} \cdot \sin \dfrac{n\pi}{l} x \cdot e^{-K n^2 \pi^2 t/l^2}.$

Therefore,

$$\frac{dy}{dx} = \frac{Ap}{l} + \frac{2}{\pi} \overset{n = \infty}{\underset{n=1}{\Sigma}} Ap \frac{(-1)^n}{n} \cdot \frac{n\pi}{l} \cdot \cos \frac{n\pi}{l} x \cdot e^{-K n^2 \pi^2 t/l^2}.$$

At the face $\qquad\qquad\qquad\qquad x = 0,$

$$\underset{x \to 0}{lt} \left(\frac{dy}{dx} \right) = \frac{Ap}{l} + \frac{2}{\pi} \overset{n = \infty}{\underset{n=1}{\Sigma}} Ap \frac{(-1)^n}{n} \cdot \frac{n\pi}{l} \cdot e^{-K n^2 \pi^2 t/l^2}.$$

Therefore volume of hydrogen emitted per second from this face

$$= K \underset{x \to 0}{lt} \left(\frac{dy}{dx} \right) = \frac{KAp}{l} \left[1 + 2 \overset{n = \infty}{\underset{n=1}{\Sigma}} (-1)^n e^{-K n^2 \pi^2 t/l^2} \right].$$

Let the hydrogen from a given area of this film be collected into a space such that

$$\frac{\text{the volume of the space}}{\text{area of film}} = V \text{ cm.},$$

i.e., the "effective depth" of the space is V cm. If this space contains no hydrogen initially and there is no leak from it, the concentration z of hydrogen in it will begin to increase steadily and we shall have

$$V \frac{dz}{dt} = \frac{KAp}{l} \left[1 + 2 \overset{n = \infty}{\underset{n=1}{\Sigma}} (-1)^n e^{-K n^2 \pi^2 t/l^2} \right].$$

Integrate this and put in the condition that $z = 0$ when $t = 0$ and we have

$$z = \frac{KAp}{Vl} \left[t + 2 \overset{n = \infty}{\underset{n=1}{\Sigma}} \frac{(-1)^n}{n^2} \cdot \frac{l^2}{K\pi^2} (1 - e^{-K n^2 \pi^2 t/l^2}) \right].$$

As t increases indefinitely the graph of y approximates to the line

$$z = \frac{KAp}{Vl} \left[t + 2 \frac{l^2}{K\pi^2} \overset{n = \infty}{\underset{n=1}{\Sigma}} \frac{(-1)^n}{n^2} \right].$$

But

$$\overset{n = \infty}{\underset{n=1}{\Sigma}} \frac{(-1)^n}{n^2} = -\frac{\pi^2}{12}.$$

Therefore the final line is

$$z = \frac{KAp}{Vl} \left[t - \frac{l^2}{6K} \right].$$

This line cuts the axis $0t$ at a time $l^2/6K$ from the time when one face is exposed to hydrogen. We shall call this time the "lag." The quantity per second emitted in the steady state we shall call the permeability.

Then permeability, $P = \dfrac{KAp}{l}$;   lag, $L = \dfrac{l^2}{6K}$,

and we have $PL = \dfrac{pl}{6}A.$

We have, then, a means of determining both the absorption coefficient A and the "diffusion constant" K.

Description of Apparatus.

The apparatus used was a modification of the Shakespear permeability tester (19) (fig. 1). This consists essentially of—

(1) An air chamber of known volume, having a flange on which the material to be tested is placed ;

(2) A hydrogen chamber, having a flange which, together with the flange on the air chamber, grips the test piece ; and

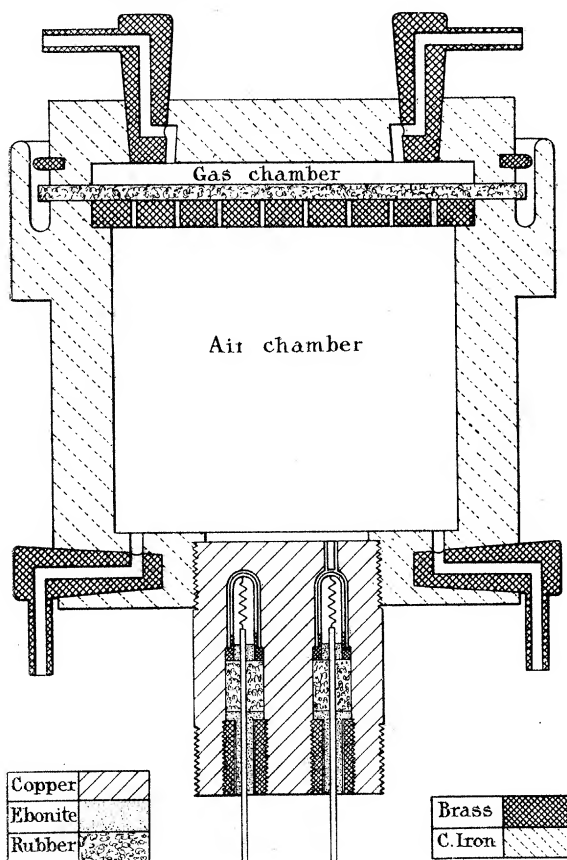| Copper |
| Ebonite |
| Rubber |

| Brass |
| C. Iron |

FIG. 1.—Vertical Section of Permeameter.

(3) A katharometer, *i.e.*, a direct reading instrument, which indicates the composition of a mixture of hydrogen and air at any given instant.

In these experiments, films were used such that the test area was a circle of 2·225 cm. diameter. The air chamber was a cylindrical vessel of cast iron, having a cylindrical hole in it about 4 cm. deep and 4 cm. in diameter. From the top it was shouldered out to a depth of about 4 mm., and on the shoulder rested a grid of brass strips, placed with their edges up, and having a square mesh of about 3 mm. side. The top of this grid was then turned flush with the top flange. This arrangement served to keep the fabric from sagging. Inlet and outlet taps opened into the bottom of this cavity.

The film was then laid on the flange and sealed. The hydrogen chamber was a cylindrical vessel of internal diameter equal to that of the top of the air chamber. It was only about 4 mm. deep. The open end was turned to rest on the flange of the air chamber, the whole lid being centred by a rim turned on the air chamber. Hydrogen could be introduced through taps which could be turned on or off by rotating the tubes through a right angle.

The katharometer was screwed into the bottom of the air chamber. It consists of a copper block containing two cylindrical holes. Into each of these holes is placed, co-axially with the hole, a platinum helix. The two helices are similar, and form two arms of a Wheatstone bridge, the other two arms being of manganin. The current in the bridge heats both helices equally, so that they are kept at a temperature 30° C. or 40° C. above the temperature of the copper block. One hole is sealed up, and the other communicates with the air chamber through small holes drilled through the end of the cell containing the helix. The bridge is adjusted to give no current through the galvanometer when both helices are in dry air. When hydrogen is admitted to one chamber, the helix in that chamber is cooled, and the resulting change in its resistance causes a deflexion of the galvanometer. In these experiments a sensitive moving coil galvanometer was used with lamp and scale, giving a sensitiveness of about 1000 divisions to 1 per cent. hydrogen in air. It was possible, therefore, to estimate, by subdivision by eye, to about one part of hydrogen in 500,000 of air.

The instrument is very quick reading. It has a time-constant of about 15 seconds.

The volume of the air chamber was measured by filling it with water and weighing the water used.

The katharometer was calibrated directly in divisions, per 1 per cent. hydrogen, by passing into it definite mixtures of hydrogen and air.

Method of Testing.

It was shown earlier in the paper that, to obtain values of K and A, we have to measure both the permeability and the lag. When hydrogen is admitted to the hydrogen chamber, and the concentration of hydrogen measured in the air chamber and plotted against time, the curve is of the form shown in fig. 2.
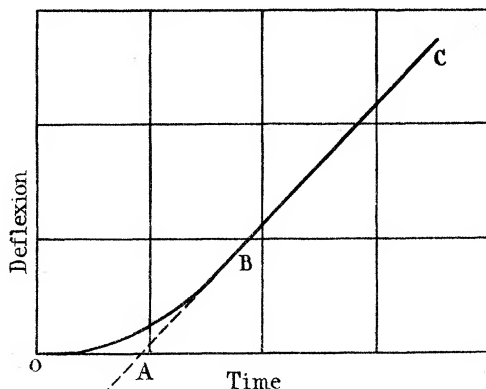

Fɪɢ. 2.—Typical Time—Deflexion Curve.

The slope of the final line BC gives us the permeability of the film, and the time represented by the distance OA is the lag.

It is necessary to consider what is the effect of the lag of the katharometer. Let v be the volume of the katharometer chamber, and let the communication holes be such that when there is a unit difference of concentration of hydrogen between inside and outside of the katharometer, q c.c. of hydrogen will escape per second.

Let
$$\frac{q}{v} = b.$$

Then, if the katharometer initially has hydrogen at a concentration z_0, and is then exposed to air, the concentration in it, at time t, will be

$$z = z_0 e^{-bt},$$

$1/b$ is called the "time constant" of the katharometer, and is the time in which the concentration will fall to $1/e$th of its initial value.

It has been shown by the writer, in a previous note on the theory of the Shakespear permeameter (20), that if the hydrogen is continuously carried away from the air chamber, while a steady state is reached in the film, and

then the air stream is suddenly stopped and the air chamber sealed, the indications of the katharometer vary with time according to the equation

$$z = \frac{P}{V} t - \frac{P}{Vb} (1 - e^{-bt}),$$

where   P = permeability of fabric,

$$V = \text{ratio} \ \frac{\text{volume of air chamber}}{\text{area of fabric}},$$

i.e., the time graph of z approximates after a time to the line

$$z = P/V \ (t - 1/b),$$

which cuts the horizontal axis at a distance $1/b$ from the origin. This gives a very convenient way of measuring $1/b$.

The case of unsteady conditions, which we are considering, is more complicated.

The volume of the katharometer is small compared with that of the air chamber, so we have to find the concentration, ω, in the katharometer at any time, t, when the katharometer is exposed to a mixture whose concentration is varying according to the equation obtained in the first part of the paper, *i.e.,*

$$z = \frac{KAp}{Vl} \left[t + 2 \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \cdot \frac{l^2}{K\pi^2} (1 - e^{-K n^2 \pi^2 t/l^2}) \right].$$

For convenience of manipulation put

$$2 \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \cdot \frac{l^2}{K\pi^2} = a,$$

and $$2 \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \cdot \frac{l^{2}}{K\pi^2} \cdot e^{-Kn^2\pi^2 t/l^2} = f(t),$$

and remember that

$$\lim_{t \to 0} f(t) = a \qquad \text{and} \qquad \lim_{t \to \infty} f(t) = 0.$$

Therefore $$z = \frac{P}{V} [t + a - f(t)].$$

Then we have

$$\frac{d\omega}{dt} = \frac{q}{v} (z - \omega) = b \left[\frac{P}{V} \{t + a - f(t)\} - \omega \right].$$

Therefore $$\frac{d}{dt} (\omega e^{bt}) = \frac{P}{V} \ b \ . \ e^{bt} [t + a - f(t)].$$

Therefore $$\omega e^{bt} + B = b \ . \ \frac{P}{V} \left[\int te^{bt} \, dt + \int ae^{bt} \, dt - \int e^{bt} f(t) \, dt \right].$$

But
$$\int t e^{bt}\, dt = \frac{1}{b} \cdot e^{bt}\left(t - \frac{1}{b}\right),$$

$$\int a e^{bt}\, dt = \frac{a}{b} e^{bt}$$

and
$$\int e^{bt} f(t)\, dt = 2 \int \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \cdot \frac{l^2}{K\pi^2} \cdot e^{(b - Kn^2\pi^2 t/l^2)}$$

$$= 2 \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \cdot \frac{l^2}{K\pi^2} \cdot \frac{e^{(b - Kn^2\pi^2 t/l^2)}}{b - Kn^2\pi^2/l^2}.$$

Therefore

$$\omega e^{bt} + B = \frac{P}{V}\left[e^{bt}\left(t - \frac{1}{b}\right) + a e^{bt} + 2b \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \frac{l^2}{K\pi^2} \frac{e^{(b - Kn^2\pi^2 t/l^2)}}{b - Kn^2\pi^2/l^2} \right].$$

When
$$t = 0, \qquad \omega = 0.$$
Therefore

$$B = \frac{P}{V}\left[-\frac{1}{b} + a + 2b \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \cdot \frac{l^2}{K\pi^2} \cdot \frac{1}{b - Kn^2\pi^2/l^2} \right]$$

and therefore

$$\omega = \frac{P}{V}\left[t - \frac{1}{b}(1 - e^{-bt}) + a(1 - e^{-bt}) + 2b \sum_{n=1}^{n=\infty} \frac{(-1)^n}{n^2} \cdot \frac{l^2}{K\pi^2} \frac{e^{-Kn^2\pi^2 t/l^2} - e^{-bt}}{b - Kn^2\pi^2/l^2} \right].$$

After a time this approximates to

$$\omega = \frac{P}{V}\left[t - \frac{1}{b} + a \right].$$

The katharometer therefore increases the lag by its own time constant, and this quantity can be measured directly by a control experiment, which is simply the permeability test when a steady state is reached.

What has here been called the lag of the katharometer includes also the lag of galvanometer and lag introduced by diffusion of hydrogen from top to bottom of the air chamber. (This is probably of the order of 2 seconds.)

The difference between the lag in the unsteady state and that in the steady state is the lag due to absorption in the rubber + the lag due to flushing the hydrogen chamber.

Lag due to Flushing of Hydrogen Chamber.

To secure uniformity of flushing with hydrogen, side tubes led off from the inlet and outlet taps of the hydrogen chamber to the two arms of a differential manometer. The rate of flow was adjusted so that the manometer indicated a difference of pressure 1 cm. of water. To ensure this rate of flow from the instant of opening the taps, the outlet led to a glass tube, or "safety bubbler," dipping just under water and from a T-piece against the inlet a

side tube led to another glass tube dipping 1 cm. under water. The following procedure was then adopted. With the inlet tap of the hydrogen chamber closed the rubber tube was detached from it and the hydrogen was allowed to run freely out at this opening so as to fill all the tubes with hydrogen right up to the tap. The rubber tube was then replaced and hydrogen then bubbled freely at the "safety bubbler" until the tap of the hydrogen chamber was turned on, when the required steady flow was established very quickly. Readings of the galvanometer were then taken every $\frac{1}{4}$ minute and plotted against time. Before the test dry air was passed above and below the film to secure drying of the rubber.

After this test a control experiment was done. The mixture at the bottom was flushed out with dry air while hydrogen was still running in the hydrogen chamber. The taps of the air chamber were then turned off at a given instant and readings again taken every quarter of a minute. The lag in this case is that of the katharometer and galvanometer and must be subtracted from the other lag to obtain that due to the absorption by the rubber and that due to flushing.

It was found that with a difference of 1 cm. of water between inlet and outlet the rate of flow of hydrogen was 4·1 c.c. per second. Since the volume of the hydrogen chamber was about 4 c.c. the lag introduced by flushing at this rate would be about 1 second. This was checked by a series of measurements of the lag in the case of a fabric when the difference of pressure between inlet and outlet was varied from 2 mm. to 18 mm. There was no difference in lag of more than 3 seconds between the extreme cases. In all calculations, therefore, 1 second is allowed for lag of flushing.

Seal between Film and Flange.

The making of a gastight seal between the film and the flanges of the permeameter presented some difficulty. At first the method which had proved successful with balloon fabrics was tried, *i.e.*, to dip the edges of the rubber in hot beeswax and vaseline up to a definite circle determined by two flat discs of iron which gripped the film. This proved unsatisfactory for two reasons :—

(1) The hot mixture caused the rubber to crinkle round the edge since there was no cotton to reinforce it; the hot mixture was also liable to alter the condition of the rubber round the edge.

(2) Too much pressure was required to press the flanges down tightly and make a gastight joint. By this pressure the film was considerably distorted.

The following methods also proved unsatisfactory :—

(*a*) Dry flanges with slight pressure.

(*b*) Vaselined flanges; vaseline spoils rubber much faster than beeswax and vaseline mixture.

(*c*) Glycerine; this made a good seal with very little pressure but the rubber film showed a tendency to slide about very easily. The glycerine also spread along the film and filled up the angles of the grid.

It was found more satisfactory to use a rubber-vaseline tap-grease with a high percentage of vaseline; 1 kgrm. load was sufficient. The grease did not tend to spread and there was very little slipping of the film. The area of specimen exposed was, therefore, that of the inside of the flange.

By a separate experiment it was found that the seal did not produce any effect on the film which would affect very seriously the permeability during the time of the test.

<div align="center">*Results.*</div>

The experiments carried out up to the present time are by no means complete or representative of the final precision of the method. No complete series of films was available and during the work minor faults appeared in the apparatus which could not be remedied before the work was postponed in favour of more direct war research. The results as they stand are, however, of interest and it is hoped to carry out more complete work later.

We have to thank Mr. A. D. Ritchie, of Kingsnorth Naval Air Station, for supplying us with the films used in this investigation. Little is known about the rubber. All three films were vulcanised (probably cold-cured) and were made from pure Para rubber. They may have been made from separate samples so that their physical properties will probably not be directly comparable. Three films were used as shown in the following Table :—

Film.	Thickness in mm.	Surface density in grm./metre^2.	Correction factor for edge-effect.
R (*a*)	1·421	1328	1·07
R (*b*)	0·657	614	1·035
R (*c*)	0·328	280	1·015

In calculating the permeability of the films from the observed rate of rise of concentration, we have to allow for the fact that the thickness of the film is appreciable when compared with the radius of the specimen. In the absence of any exact estimate of the disturbance in the lines of flow at the edge of the specimen it is assumed that the effective addition to the radius is not less than zero and not more than the thickness of the film. Half the

thickness of the film is added to the radius in all cases so as to give an approximation. Taking the radius of the specimen as approximately 20 mm. we have the correcting factor F for edge effect as given in the above Table.

In calculating the constant of the permeameter we use the following data :—

Volume of permeameter............ 50·1 c.c.

Area of film .... 15·55 cm².

Sensitiveness of katharometer ... 905 div. to 1 per cent. hydrogen in air at 20° C.

$$\text{Therefore 1 div. per min.} = \frac{50 \cdot 1}{100 \times 905 \times 15 \cdot 55 \times 60} \text{ c.c./cm.}^2 \text{ sec.}$$

$$= 5 \cdot 94 \times 10^{-7} \text{ cm./sec.,}$$

i.e., we multiply div. per min, by $5 \cdot 94 \times 10^{-7}$ to get permeability in cm./sec.

Two other corrections have to be applied for temperature.

(*a*) The katharometer decreases in sensitiveness by 0·002 per 1° C. rise in temperature. To reduce all results to 20° C., div./min. are multiplied by $1 + 0 \cdot 002(\theta - 20)$.

(*b*) The permeameter measures volumes of hydrogen in cubic centimentres at the temperature of the experiment. For convenience all results are compared at 20° C., so in calculating permeabilities, div./min. are divided by $1 + 0 \cdot 0037(\theta - 20)$.

The combination of these two corrections is to divide div./min. by $1 + 0 \cdot 0017(\theta - 20)$.

The following Table shows results of tests on the three films described and includes rate of movement of galvanometer, lag after subtracting lag of control experiment and 1 second for flushing the hydrogen chamber, and temperature of test :—

Film.	Div./min.	Temperature.	Lag.	Permeability.	
R (*a*)	4·49	° C. 16·1	319	$2 \cdot 51 \times 10^{-6}$	Constant
	5·04	19·5	293	$2 \cdot 80 \times 10^{-6}$	$\dfrac{5 \cdot 94 \times 10^{-7}}{1 \cdot 07 (1 + 0 \cdot 0017\theta - 20)}$
	5·76	22·8	260	$3 \cdot 18 \times 10^{-6}$	Thickness = 1·421 mm.
R (*b*)	9·11	16·3	76 (69)	$5 \cdot 20 \times 10^{-6}$ $(5 \cdot 90 \times 10^{-6})$	Constant $\dfrac{5 \cdot 94 \times 10^{-7}}{1 \cdot 033 (1 + 0 \cdot 0017\theta - 20)}$ Thickness = 0·657 mm.
R (*c*)	21·0	19·1	14	$12 \cdot 27 \times 10^{-6}$	Constant
	21·1	19·4	16	$12 \cdot 32 \times 10^{-6}$	$\dfrac{5 \cdot 94 \times 10^{-7}}{1 \cdot 015 (1 + 0 \cdot 0017\theta - 20)}$
	23·2	21·2	10	$13 \cdot 51 \times 10^{-6}$	Thickness = 0·328 mm.

P, L, and PL are plotted against θ for R(a) in graphs I, II, and III respectively (fig. 3).
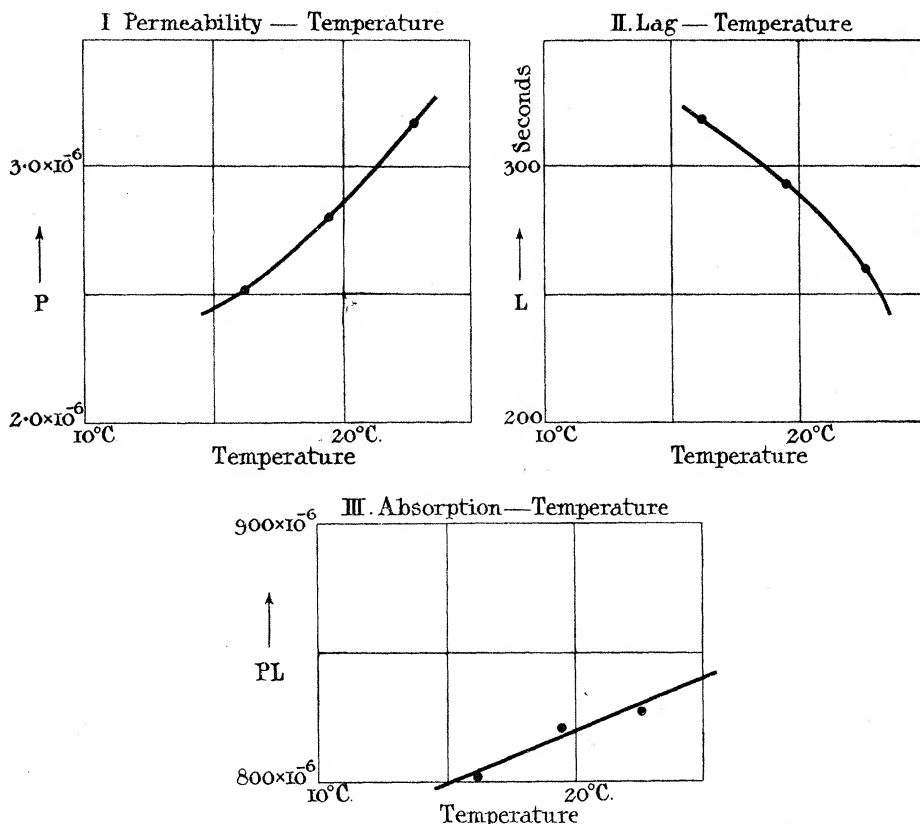

Fig. 3.—Relations between Permeability, Lag, and Temperature of Film.

The figures for P and L in brackets are those estimated for a temperature of 20° C., using the temperature curves of P and L for R(a) to obtain the correction.

Now, if the principles stated at the beginning of the paper hold, and if the rubbers in the different films are physically similar, we should expect the following relations to hold between permeability, lag, and permeability × lag, on the one hand, and thickness on the other :—

$$P l = \mathrm{K A} p, \qquad \frac{\mathrm{L}}{l^2} = \frac{1}{6\,\mathrm{K}}, \qquad \frac{\mathrm{PL}}{l} = \frac{p\mathrm{A}}{6},$$

all the quantities on the right-hand side being independent of l, the thickness of the film.

In the following table data are given for a temperature of 20° C., to enable these relations to be tested :—

Film.	l.	l^2.	P.	$\dfrac{1}{P}$	L.
	cm.	cm^2.			secs.
R (a)	0·1421	2·02 × 10^{-2}	2·85 × 10^{-6}	0·351 × 10^6	287
R (b)	0·0657	0·432 × 10^{-2}	5·90 × 10^{-6}	0·169 × 10^6	69
R (c)	0·0328	0·108 × 10^{-2}	12·8 × 10^{-6}	0·0782 × 10^6	13·3

	PL.	Pl.	$\dfrac{L}{l^2}$	$\dfrac{PL}{l}$
R (a)	818 × 10^{-6}	0·405 × 10^{-6}	14,200	5760 × 10^{-6}
R (b)	407 × 10^{-6}	0·388 × 10^{-6}	16,000	6200 × 10^{-6}
R (c)	170 × 10^{-6}	0·420 × 10^{-6}	12,300	5180 × 10^{-6}

The quantities 1/P, L, and PL are plotted against l, l^2, and l respectively, in graphs IV, VI, and VII (fig. 4).

IV. $\dfrac{1}{\text{Permeability}}$—Thickness.

VI. Lag—(Thickness)^2.
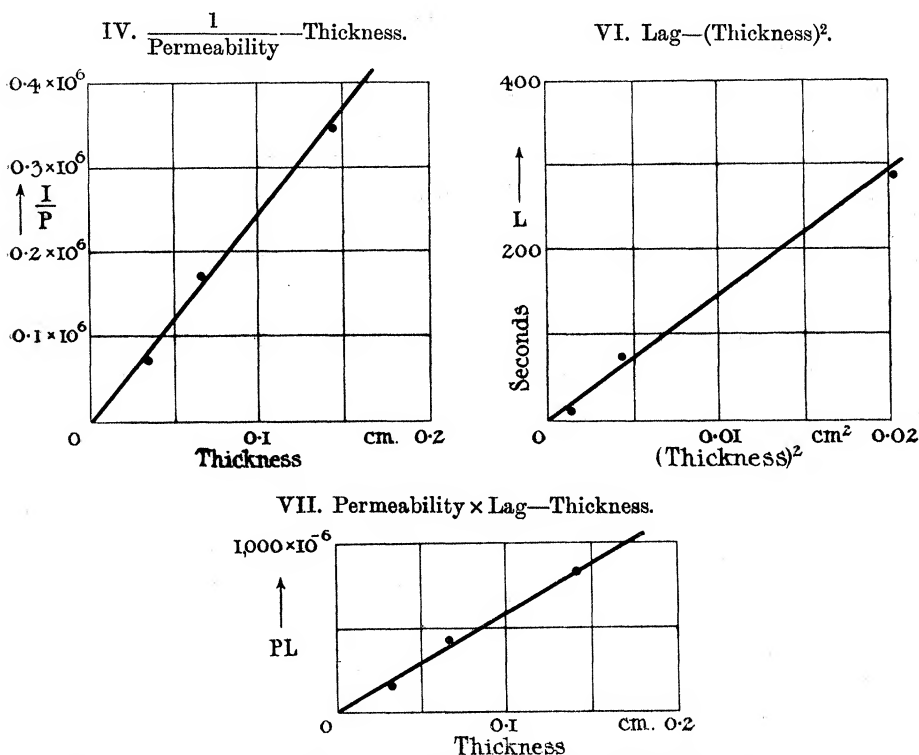
VII. Permeability × Lag—Thickness.

FIG. 4.—Relations between Permeability, Lag, and Thickness of Film at 20° C.

It will be seen from the Table that the quantities Pl, L/l^2 and PL/l, though different for different films, show no regular variation with l.

From the graphs V, VI, and VII slopes of lines give mean values as follows :—

$$\frac{L}{l^2} = 1\cdot46 \times 10^4, \quad \text{Therefore } K = \frac{1}{6 \times 1\cdot46 \times 10^4} = 11\cdot4 \times 10^{-6} \text{ cm}^2/\text{sec.,}$$

$$\frac{PL}{l} = 5\cdot3 \times 10^{-3} \qquad \text{and } A = \frac{6\,PL}{l} = 3\cdot5 \times 10^{-2}.$$

Graph III shows PL plotted against temperature, to show how the absorption coefficient depends on temperature. This shows a temperature coefficient at 20° C. of +0·5 per cent./1° C.

Conclusions.

1. The behaviour of the set of rubber films agrees in all respects, within the limits of error of the experiments, with that predicted from certain assumptions of a simple process of diffusion through a rubber membrane. The conclusion previously reached, that the surface resistance is negligible, is confirmed.

2. The method gives a quick and satisfactory means of measuring the absorption and diffusion-constant of a material for a gas, and is capable of development with greater precision.

3. The mean value for the diffusion-constant for the three films considered was $11\cdot4 \times 10^{-6}$ cm.-sec. at 20° C. The actual values for the three films separately were $11\cdot7 \times 10^{-6}$, $10\cdot4 \times 10^{-6}$, and $13\cdot6 \times 10^{-6}$ cm.-sec. (The last value is not so precise as the others.)

4. The mean value of the absorption coefficient was 0·035 at normal pressure and 20° C. The actual values for the three films were 0·035, 0·037, and 0·031. (The last value is not so precise as the others.)

5. The coefficient of absorption has a low temperature coefficient (approximately 0·5 per cent./1° C.), compared with that of the diffusion constant. It is not that which is responsible for the great variation of permeability with temperature. This suggests that the process of absorption is a simple molecular action.

Passage of other Gases through Rubber.

The method used for hydrogen has been applied to the study of hydrogen, nitrogen, oxygen, carbon dioxide, nitrous oxide, and ammonia.

The film used for these gases was in all cases about 0·4 mm. thick and all the films were cut from the same sheet.

In every case the time taken to reach a steady state was longer than for hydrogen, so the length of each test and the intervals between tests were necessarily longer. Not many tests, therefore, could be made on any parti-

cular film, as the permeability changed appreciably through edge effect of the sealing mixture within a single day. Good temperature curves were impossible, and in some cases it was impracticable even to make confirmatory tests. For the same reason, all the gases could not be tested on the same film, but of each film a test was taken with hydrogen, as a means of reference from one film to another. All tests were made at 17° C., as nearly as possible.

Special difficulties were met with oxygen, nitrogen, and ammonia.

The katharometer is not very sensitive to oxygen or nitrogen in air, so a special katharometer was used to show small traces of these gases in hydrogen. Hydrogen was then used instead of air as the gas into which the oxygen or nitrogen permeated. With this arrangement, the "natural leak" of the permeameter becomes very much more important. It was found that this leak was of the same order as the leak of air to be observed. To determine this leak as accurately as possible, readings were taken first with hydrogen flowing above and below the film. An approximately steady deflection was soon produced. The bottom chamber was then closed by the taps and the readings continued. The slope of the line, when readings were plotted against time, gave the natural leak of the permeameter. After this had continued sufficiently to determine the slope, the top chamber was flushed out with the gas to be examined by the same method as was used for hydrogen. The increase in the rate of movement of the galvanometer showed the extra leakage through the rubber. In measuring the lag it was necessary to note the point of intersection of the final line with the initial line with the original line (which showed the natural leakage) produced, not with the horizontal line through the reading at the time of introduction of the oxygen or nitrogen. A considerable part of the natural leak was probably due to the emission of absorbed air and water in the permeameter and film, and this emission was not constant. This greatly increased the difficulty of accurate measurement. It was not possible to dry out for a sufficient time to eliminate the effect, because of the edge deterioration of the rubber. The results on nitrogen, oxygen, and air are, therefore, of a much lower order of precision than the others. In fact, the leakage of nitrogen alone was not detectable, but those of oxygen and air were measurable. (Oxygen diffuses through rubber about twice as rapidly as nitrogen.)

The special difficulties with ammonia were due to :—

1. The low sensitiveness of the katharometer to ammonia ;

2. The peculiar shape of the calibration curve of the katharometer for ammonia in air ; and

3. The great length of time taken by the test.

The deflection for 1 per cent. of ammonia is only about one-tenth of that

for 1 per cent. of hydrogen. It is in the same direction for small percentages but reaches a maximum, then zero, and finally at 100 per cent. ammonia a deflection in the opposite direction. The permeability to the gas is very high, so that in two hours there is a large percentage of ammonia in the bottom of the permeameter, and the curvature due to the calibration curve becomes very marked and back diffusion is considerable. But, by this time, steady conditions are not nearly reached, so there is no final straight line to produce back to cut the horizontal axis. Corrections have been applied so far as possible, and the given estimate of the lag is probably correct within 10 per cent.

The lag of the katharometer is due to the slowness of diffusion through the holes leading to the sensitive helix. It depends on the diffusion-constant of the gas, so separate control experiments had to be made with each gas.

The katharometer had also to be calibrated with each gas used by passing through it mixtures of known composition.

The results obtained are shown in the following Table. Where two or three confirmatory tests could be made the figure given is the mean of them :—

Film.	Thickness.	Gas.	Temperature.	Rate of galvanometer movement.	Total lag.	Katharometer lag.	Rubber lag.	Deflection per 1 per cent. of gas.
[1]	cm. $4 \cdot 29 \times 10^{-2}$	H_2 CO_2	° C. $17 \cdot 3$ $17 \cdot 6$	div./min. $11 \cdot 7$ $4 \cdot 17$	secs. 65 495	secs. $29 \cdot 5$ 134	secs. $35 \cdot 5$ 361	1001 -132
[2]	$4 \cdot 12 \times 10^{-2}$	H_2 N_2O H_2	$16 \cdot 0$ $17 \cdot 0$ $16 \cdot 6$	$11 \cdot 8$ $7 \cdot 3$ $11 \cdot 8$	73 516 73	31 120 31	42 396 42	1001 -134 1001
[3]	$4 \cdot 55 \times 10^{-2}$	Air O_2	$17 \cdot 2$ $17 \cdot 2$	$0 \cdot 46$ $0 \cdot 76$	317 383	[31] [31]	286 352	217 205
[4]	$4 \cdot 12 \times 10^{-2}$	H_2 NH_3	$17 \cdot 3$ $17 \cdot 4$	$12 \cdot 2$ $10 \cdot 05$	74 3960	29 120	45 3840	1001 $82 \cdot 3$

The values given in brackets are not direct experimental values but the mean of all those obtained for small quantities of hydrogen in air, this being very nearly the same as for small quantities of air in hydrogen.

The interpretation of these results in terms of permeability, absorption coefficient, and diffusion-constant is shown in the following Table. The product Pl is permeability reduced to a film of unit thickness. The first three columns give results in absolute units, the second three give the relative values, those for hydrogen being unity.

In the case of film (4) the values for hydrogen are the means of those obtained on the other films since the conditions of the experiment would not allow a direct test.

Gas.	Diffusion constant.	Absorption coefficient.	Permeability.
H_2	$7 \cdot 23 \times 10^{-6}$ (mean)	$0 \cdot 0397$	$26 \cdot 7 \times 10^{-8}$
CO_2	$0 \cdot 85 \times 10^{-6}$	$0 \cdot 86$	$73 \cdot 4 \times 10^{-8}$
N_2O	$0 \cdot 72 \times 10^{-6}$	$1 \cdot 71$	$121 \cdot 0 \times 10^{-8}$
Air	$1 \cdot 21 \times 10^{-6}$	$0 \cdot 043$	$5 \cdot 18 \times 10^{-8}$
O_2	$0 \cdot 95 \times 10^{-6}$	$0 \cdot 091$	$8 \cdot 97 \times 10^{-8}$
NH_3	$0 \cdot 074 \times 10^{-6}$	$41 \cdot 0$	$303 \cdot 0 \times 10^{-8}$

Gas	Relative K.	Relative A.	Relative Pl.	Relative solubility in water at 15° C.	Critical temperature.
					° C.
H_2	$1 \cdot 00$	$1 \cdot 00$	$1 \cdot 00$	$1 \cdot 00$	-238
CO_2	$0 \cdot 098$	$27 \cdot 6$	$2 \cdot 73$	$52 \cdot 0$	$+31$
N_2O	$0 \cdot 107$	$44 \cdot 0$	$4 \cdot 62$	$41 \cdot 5$	$+37$
Air	$0 \cdot 168$	$1 \cdot 08$	$0 \cdot 19$	$0 \cdot 95$	—
O_2	$0 \cdot 135$	$2 \cdot 30$	$0 \cdot 336$	$1 \cdot 60$	-119
NH_3	$0 \cdot 0117$	950	$11 \cdot 3$	40000	$+131$

The lag of 64 minutes for ammonia is very striking. This means that in a film of 1 mm. thickness gradients would not reach within 1 per cent. of their final values in less than eight hours. For a thickness of 1 cm. a month would be required.

It will be seen from these figures that, although some of these gases have for some time been known to pass through rubber membranes more rapidly than hydrogen, in no case is it because the material itself is more permeable to them when the melecular concentrations are the same. On the contrary, ammonia has an abnormally low diffusion constant, even after allowance is made for its greater density, as shown by the following Table :—

Gas.	Approximate relative density.	$\sqrt{d}$.	Relative K.	$K\sqrt{d}$.
H_2	2	$1 \cdot 4$	$1 \cdot 00$	$1 \cdot 4$
CO_2	48	$6 \cdot 9$	$0 \cdot 098$	$0 \cdot 67$
N_2O	44	$6 \cdot 6$	$0 \cdot 107$	$0 \cdot 70$
Air	$14 \cdot 4$	$3 \cdot 8$	$0 \cdot 168$	$0 \cdot 64$
O_2	16	$4 \cdot 0$	$0 \cdot 135$	$0 \cdot 54$
NH_3	17	$4 \cdot 1$	$0 \cdot 0117$	$0 \cdot 048$

Thus, viewed in the light of Graham's Law of Diffusion, hydrogen has an abnormally high and ammonia an abnormally low diffusion-constant.

The last two columns are added to bring out the general resemblance between absorption of gases by rubber and by water, and to support the suggestion that the absorption of gases by rubber has some close connection with the nearness of the gas to its critical state.   If the latter is the case we should expect that with increase of pressure the absorption, and hence the permeability, to increase more rapidly than the partial pressure of the gas. Such an effect has been observed with carbon dioxide by Prof. Dewar (21), but as the rubber film was supported on gauze with high pressure on one side it is not improbable that some of the effect at least was due to local thinning of the film due to its moulding into the irregularities of the gauze.

The similarity between the solubilities of these gases in rubber and in water may have another explanation.   Prof. Dewar (22) has shown that the logarithm of the permeability of rubber to a gas varies linearly with the temperature of the rubber, but that there are different slopes of the line above and below 0° C. suggesting that absorbed water has some definite function in determining the permeability.   It is also known that rubber absorbs a large quantity of water vapour and is very permeable to it.   The high concentration of ammonia and other gases in rubber may possibly, then, be due to their solution by the absorbed water.

It seems clear that the process of diffusion of a gas through a rubber film is determined by two more or less separate processes.   Neither of these obeys simple laws.   We can hardly expect, therefore, to go very far in our understanding of the problem by studying permeability alone.   Measurements must be made simultaneously on the permeability, absorption coefficient, and diffusion-constant, or, as a minimum, any two of these three quantities.

REFERENCES.

(1) Wroblewski, 'Wied. Annalen der Physik,' vol. 8 (1879).
(2) Draper and Mitchell, 'Roy. Inst. Proc. on Prof. Graham's Scientific Work,' 1870 to 1872.
(3) Wroblewski, *loc. cit.*
(4) Hüfner, 'Wied. Annalen der Physik,' 1888.
(5) Wroblewski, *loc. cit.*
(6) Barr, 'Technical Reports, Adv. Com. for Aeronautics.'
(7) Shakespear, unpublished.
(8), (9) Shakespear, "On the Permeability of Films and of Proofed Fabrics," 'Adv. Com. for Aeronautics,' T. 1164, June, 1918.

(10), (11), (12) Shakespear, unpublished.

(13), (15), (16), (17) Shakespear, Daynes and Lambourn, " A Brief Account of some Experiments on the Permeability of Balloon Fabrics to Air," ' Advisory Committee for Aeronautics.'

(14) Dewar, ' Proc. Roy. Inst.,' March, 1918.

(18) Carslaw, ' Fourier's Series and Integrals,' p. 263 (1906).

(19) Shakespear, ' A New Permeability Tester for Balloon Fabrics.' Advisory Committee of Aeronautics.

(20) Shakespear and Daynes, " Further Notes on the Hydrogen Permeameter," ' Reports of Advisory Committee for Aeronautics.'

(21), (22) Dewar, see (13).

On the Structure of the Balmer Series of Hydrogen Lines.

By T. R. MERTON, M.A., D.Sc.

Introductory.

It is well known that the spectrum of hydrogen comprises the series of lines generally known as the Balmer series, which is a prominent feature in the spectra of the stars and nebulæ, and the secondary spectrum, consisting of a vast number of lines whose presence in celestial spectra has not yet been established.   The co-ordination of the secondary spectrum would appear to present great difficulties on account of its complexity, but it is perhaps remarkable that a precise knowledge of the Balmer series, which was at one time considered to be the most simple series known in spectroscopy, should still be wanting.

Balmer showed, at a time when the complexity of the lines was not yet known, that the wave-lengths could be represented with considerable accuracy by the formula $\lambda = 3646 \cdot 14 m^2/(m^2 - 4)$, where m takes successive integral values.   Balmer's formula is a special case of the formula of Rydberg for the wave-number $\nu = N [1/(2 + p)^2 - 1/(m + q)^2]$, where ν is the wave-number, N Rydberg's " universal " constant, and p and q are fractions appropriate to the series; this is identical with Balmer's formula when p and q are put equal to zero.   Curtis* has deduced from a series of accurate measurements of the leading lines of the Balmer series that the value of Rydberg's constant N is equal to 109678·3, and that the wave-numbers of the lines cannot be represented to the degree of accuracy attained in his

* ' Roy. Soc. Proc.,' vol. 90, p. 605 (1914) ; vol. 96, p. 147 (1919).